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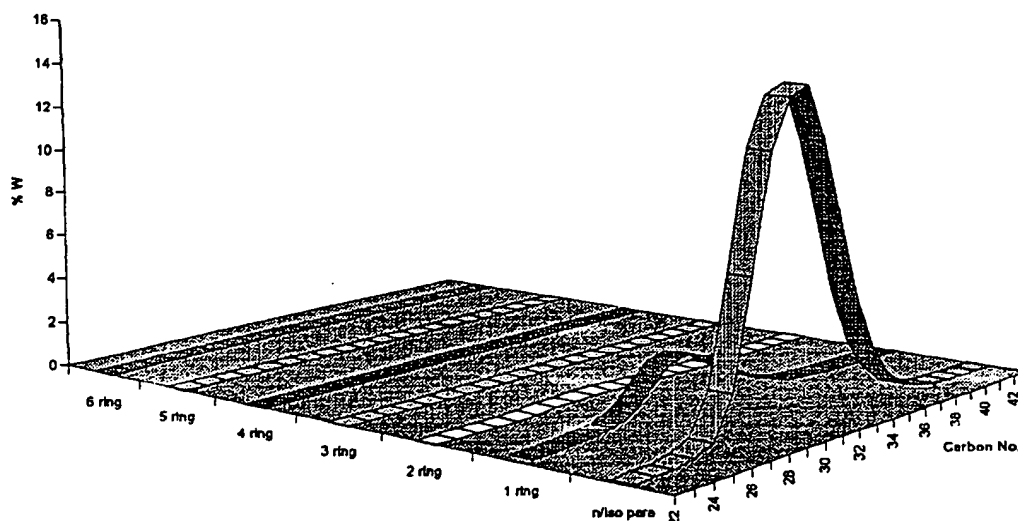
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(54) Title: AUTOMATIC TRANSMISSION FLUID



(57) Abstract: Automatic transmission fluid having a kinematic viscosity at 100 °C of between more than 4 and 10 cSt, a dynamic viscosity at -40 °C of less than 10000 mPas comprising an additive package and a base oil, wherein the base oil fraction comprises at least 98 wt% saturates, of which saturates fraction the content of cyclo-paraffins is between 10 and 40 wt% and wherein the pour point of the base oil is less than -25 °C.

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## AUTOMATIC TRANSMISSION FLUID

The invention is directed to an automatic transmission fluid having a kinematic viscosity at 100 °C of between more than 4 and 10 cSt, a dynamic viscosity at -40 °C of less than 10000 mPas comprising an additive package and a base oil component, wherein the base oil component comprises at least 98 wt% saturates, of which saturates fraction the content of cyclo-paraffins is between 10 and 40 wt% and wherein the pour point of the base oil component is less than -25 °C.

WO-A-9941332 discloses such an automatic transmission fluid composition. The base oil component of this composition was obtained by hydroisomerisation of a hydrotreated slack wax followed by solvent dewaxing. The pour point of the base oil was about -23 °C, which is a typical pour point for base oils as obtained by means of a solvent dewaxing process.

A disadvantage of the ATF fluid as disclosed in WO-A-9941332 is their unfavourable low temperature performance, for example expressed in their low temperature Brookfield viscosity performance.

Applicants found that with the above-described formulation these disadvantages have been overcome.

Automatic transmission fluids (ATF's) are divided into two main groups, friction modified fluids and non-friction modified fluids and are used in automotive and commercial vehicle service. The friction modified and non-friction modified fluids are generally similar in their basic requirements; high thermal and oxidation resistance, low temperature fluidity, high compatibility, foam control, corrosion control and anti-wear properties. Both types of fluids have similar friction properties at

high sliding speeds. Different automatic transmission manufacturers do require somewhat different properties in the fluids used as sliding speed approaches zero (clutch lock-up). Some manufacturers specify that the ATF's used with their transmissions exhibit a decrease in friction coefficient (i.e., more slipperiness) while others want an increase in friction coefficient.

The Automatic Transmission Fluid according to the present invention will preferably contain detergents, dispersants, anti-wear, anti-rust, friction modifiers, anti-foaming agents, a detergent-inhibitor pack, a viscosity index (VI) improver, seal sweller and a pour point depressant. The amount of additives will depend on the specific additives and combination used and the specific required properties as specified below in more detail.

Preferably the frictional behaviour of the fluid is adjusted to specific requirements to guaranty safe power transfer and shift performance at low and high sliding speeds. The fully formulated fluid is further suitably compatible with synthetic rubber seals used in automatic transmissions. The kinematic viscosity (cSt) is preferably between 30 and 60 at 40 °C, and between about 4 to 10 at 100 °C; Brookfield viscosity of below 20000 mPas at -40 °C, 10000 mPas at about -26 to -40 °C, flash points (COC) between about 150 to about 220 °C; pour point between about -36 to -48 °C.

The base oil fraction in the Automatic Transmission Fluid according to the invention is the base oil as described above and optionally one or more additional base oils. Possible additional base stocks are mineral base oils and synthetic base oils. Suitable synthetic base oils are the so-called poly-alpha olefins base stocks. The improved solvency properties of the basic base oil of the presently claimed fluid will enhance the

20 pas  
200 poise  
20000 cpoise

lesser solvency properties of the poly-alpha olefin base stock, while taking advantage of the viscometric properties of the poly-alpha olefin. The advantages of the present invention are however fully appreciated when  
5 the base oil fraction in the claimed fluid comprises of more than 80 wt%, preferably more than 90 wt% and most preferably 100 wt% of the basic and novel base oil component as described in this application.

The base oil component of the automatic transmission  
10 fluid according to the present invention has not been disclosed in the prior art and it is this novel base oil component, which provides the advantages as, described above. Known from WO-A-0014179, WO-A-0014183, WO-A-0014187 and WO-A-0014188 are lubricant base stock  
15 comprising at least 95 wt% of non-cyclic isoparaffins. WO-A-0118156 describes a base oil derived from a Fischer-Tropsch product having a naphthenics content of less than 10%. Also the base oils as disclosed in applicant's patent applications EP-A-776959 or EP-A-668342 have been  
20 found to comprise less than 10 wt% of cyclo-paraffins. Applicants repeated Example 2 and 3 of EP-A-776959 and base oils were obtained, from a waxy Fischer-Tropsch synthesis product, wherein the base oils consisted of respectively about 96 wt% and 93 wt% of iso- and normal  
25 paraffins. Applicants further prepared a base oil having a pour point of -21 °C by catalytic dewaxing a Shell MDS Waxy Raffinate (as obtainable from Shell MDS Malaysia Sdn Bhd) using a catalyst comprising synthetic ferrierite and platinum according to the teaching of EP-A-668342 and  
30 found that the content of iso- and normal paraffins was about 94 wt%. Thus these prior art base oils derived from a Fischer-Tropsch synthesis product had at least a cyclo-paraffin content of below 10 wt%. Furthermore the base oils as disclosed by the examples of application  
35 WO-A-9920720 will not comprise a high cyclo-paraffin

content. This because feedstock and preparation used in said examples is very similar to the feedstock and preparation to prepare the above prior art samples based on EP-A-776959 and EP-A-668342.

5           The lubricating base oil component comprises preferably at least 98 wt% saturates, more preferably at least 99.5 wt% saturates and most preferably at least 99.9 wt%. This saturates fraction in the base oil component comprises between 10 and 40 wt% of cyclo-  
10       paraffins. Preferably the content of cyclo-paraffins is less than 30 wt% and more preferably less than 20 wt%. Preferably the content of cyclo-paraffins is at least 12 wt%. The unique and novel base oils are further  
15       characterized in that suitably the weight ratio of 1-ring cyclo-paraffins relative to cyclo-paraffins having two or more rings is greater than 3 preferably greater than 5. It was found that this ratio is suitably smaller than 15.

          The cyclo-paraffin content as described above is measured by the following method. Any other method  
20       resulting in the same results may also be used. The base oil sample is first separated into a polar (aromatic) phase and a non-polar (saturates) phase by making use of a high performance liquid chromatography (HPLC) method IP368/01, wherein as mobile phase pentane is used instead  
25       of hexane as the method states. The saturates and aromatic fractions are then analyzed using a Finnigan MAT90 mass spectrometer equipped with a Field desorption/Field Ionisation (FD/FI) interface, wherein FI (a "soft" ionisation technique) is used for the semi-  
30       quantitative determination of hydrocarbon types in terms of carbon number and hydrogen deficiency. The type classification of compounds in mass spectrometry is determined by the characteristic ions formed and is normally classified by "z number". This is given by the  
35       general formula for all hydrocarbon species:  $C_nH_{2n+z}$ .

Because the saturates phase is analysed separately from the aromatic phase it is possible to determine the content of the different (cyclo)-paraffins having the same stoichiometry. The results of the mass spectrometer are processed using commercial software (poly 32; available from Sierra Analytics LLC, 3453 Dragoo Park Drive, Modesto, California GA95350 USA) to determine the relative proportions of each hydrocarbon type and the average molecular weight and polydispersity of the saturates and aromatics fractions.

The base oil component preferably has a content of aromatic hydrocarbon compounds of less than 1 wt%, more preferably less than 0.5 wt% and most preferably less than 0.1 wt%, a sulphur content of less than 20 ppm and a nitrogen content of less than 20 ppm. The pour point of the base oil is preferably less than -30 °C and more preferably lower than -40 °C. The viscosity index is higher than 120. It has been found that the novel base oils typically have a viscosity index (VI) of below 150 and a dynamic viscosity at -40 °C of between 3000 and 6000 cP. The kinematic viscosity at 100 °C of the base oil component is preferably between 3.5 and 6 cSt and the Noack volatility is preferably between 6 and 14 wt%. The flash point (COC) is preferably above 140 °C.

Applicants found that the above base oil component is obtainable according to the following process wherein the following steps are performed:

(a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic Fischer-Tropsch product, which product has a weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product of at least 0.2 and

wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms

(b) hydrocracking/hydroisomerising the Fischer-Tropsch product,

5 (c) separating the product of step (b) into one or more gas oil fractions, a base oil precursor fraction and a optionally a higher boiling fraction,

(d) performing a pour point reducing step to the base oil precursor fraction obtained in step (c), and

10 (e) recovering the base oil component from the effluent of step (d).

Step (a) is preferably performed by making use of a specific catalyst in order to obtain the relatively heavy Fischer-Tropsch product. The Fischer-Tropsch catalyst is  
15 suitably a cobalt-containing catalyst as obtainable by (aa) mixing (1) titania or a titania precursor, (2) a liquid, and (3) a cobalt compound, which is at least partially insoluble in the amount of liquid used, to form a mixture; (bb) shaping and drying of the mixture thus  
20 obtained; and (cc) calcination of the composition thus obtained.

Preferably at least 50 weight percent of the cobalt compound is insoluble in the amount of liquid used, more preferably at least 70 weight percent, and even more  
25 preferably at least 80 weight percent, and most preferably at least 90 weight percent. Preferably the cobalt compound is metallic cobalt powder, cobalt hydroxide or an cobalt oxide, more preferably  $\text{Co}(\text{OH})_2$  or  $\text{Co}_3\text{O}_4$ . Preferably the cobalt compound is used in an  
30 amount of up to 60 weight percent of the amount of refractory oxide, more preferably between 10 and 40 wt percent. Preferably the catalyst comprises at least one promoter metal, preferably manganese, vanadium, rhenium, ruthenium, zirconium, titanium or chromium, most  
35 preferably manganese. The promoter metal(s) is preferably

used in such an amount that the atomic ratio of cobalt and promoter metal is at least 4, more preferably at least 5. Suitably at least one promoter metal compound is present in step (aa). Suitably the cobalt compound is  
5 obtained by precipitation, optionally followed by calcination. Preferably the cobalt compound and at least one of the compounds of promoter metal are obtained by co-precipitation, more preferably by co-precipitation at constant pH. Preferably the cobalt compound is  
10 precipitated in the presence of at least a part of the titania or the titania precursor, preferably in the presence of all titania or titania precursor. Preferably the mixing in step (aa) is performed by kneading or mulling. The thus obtained mixture is subsequently shaped  
15 by pelletising, extrusion, granulating or crushing, preferably by extrusion. Preferably the mixture obtained has a solids content in the range of from 30 to 90% by weight, preferably of from 50 to 80% by weight. Preferably the mixture formed in step (aa) is a slurry  
20 and the slurry thus-obtained is shaped and dried by spray-drying. Preferably the slurry obtained has a solids content in the range of from 1 to 30% by weight, more preferably of from 5 to 20% by weight. Preferably the calcination is carried out at a temperature between 400  
25 and 750 °C, more preferably between 500 and 650 °C. Further details are described in WO-A-9934917.

The process is typically carried out at a temperature in the range from 125 to 350 °C, preferably 175 to 275 °C. The pressure is typically in the range from 5 to  
30 150 bar abs., preferably from 5 to 80 bar abs., in particular from 5 to 50 bar abs. Hydrogen (H<sub>2</sub>) and carbon monoxide (synthesis gas) is typically fed to the process at a molar ratio in the range from 0.5 to 2.5. The gas hourly space velocity (GHSV) of the synthesis gas in the  
35 process of the present invention may vary within wide



ranges and is typically in the range from 400 to 10000 Nl/l/h, for example from 400 to 4000 Nl/l/h. The term GHSV is well known in the art, and relates to the volume of synthesis gas in Nl, i.e. litres at STP conditions (0 °C and 1 bar abs), which is contacted in one hour with one litre of catalyst particles, i.e. excluding interparticular void spaces. In the case of a fixed catalyst bed, the GHSV may also be expressed as per litre of catalyst bed, i.e. including interparticular void space. Step (a) can be performed in a slurry reactor or preferably in a fixed bed. Further details are described in WO-A-9934917.

The Fischer-Tropsch product obtained in step (a), optionally after separating some of the lower boiling compounds, for example the compounds having 4 carbon atoms or less and any compounds having a boiling point in that range, is used in step (b). This product has at least 30 wt%, preferably at least 50 wt% and more preferably at least 55 wt%, of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is at least 0.2, preferably at least 0.4 and more preferably at least 0.55. Preferably the Fischer-Tropsch product comprises a C<sub>20</sub><sup>+</sup> fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. The initial boiling point of the Fischer-Tropsch product may range up to 400 °C, but is preferably below 200 °C.

The Fischer-Tropsch product as described in detail above suitably has a content of non-branched compounds of above 80 wt%. In addition to the Fischer-Tropsch product obtained in step (a) also other fractions may be

additionally processed in step (b). A possible other fraction may suitably be the higher boiling fraction obtained in step (c) or part of said fraction.

5       The Fischer-Tropsch product will contain no or very little sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limit, which is currently 1 ppm for  
10       nitrogen and 5 ppm for sulphur.

      The Fischer-Tropsch product can optionally be subjected to a mild hydrotreatment step before performing step (b) in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of  
15       the Fischer-Tropsch reaction. Such a hydrotreatment is described in EP-B-668342.

      The hydrocracking/hydroisomerisation reaction of step (b) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen  
20       from those known to one skilled in the art as being suitable for this reaction. Catalysts for use in step (b) typically comprise an acidic functionality and a hydrogenation/dehydrogenation functionality. Preferred acidic functionalities are refractory metal oxide  
25       carriers. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly  
30       preferred catalyst comprises platinum or platinum/palladium supported on a silica-alumina carrier. If desired, applying a halogen moiety, in particular fluorine, or a phosphorous moiety to the carrier, may enhance the acidity of the catalyst carrier. Examples of  
35       suitable hydrocracking/hydroisomerisation processes and

suitable catalysts are described in WO-A-0014179, EP-A-532118, EP-B-666894 and the earlier referred to EP-A-776959. The hydrocracking catalyst may also contain a molecular sieve as for example described in  
5 US-A-5362378.

Preferred hydrogenation/dehydrogenation functionalities are Group VIII non-noble metals, for example nickel and cobalt and Group VIII noble metals, for example palladium and more preferably platinum or  
10 platinum/palladium alloys. The catalyst may comprise the hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst  
15 for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the  
20 catalyst. The binder can be non-acidic. Examples are clays and other binders known to one skilled in the art.

In step (b) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range  
25 of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be  
supplied at a gas hourly space velocity of from 100 to  
30 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The  
ratio of hydrogen to hydrocarbon feed may range from 100  
35 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (b) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 65 wt%. The feed as used above in the definition is the total hydrocarbon feed fed to step (b), thus also any optional recycles, such as the optional higher boiling fraction as obtained in step (c).

In step (c) the product of step (b) is separated into one or more gas oil fractions, a base oil precursor fraction having preferably a T10wt% boiling point of between 200 and 450 °C. If also a higher boiling fraction is isolated in step (c) the T90wt% boiling point of the base oil precursor fraction is preferably between 300 and 650 preferably 550 °C.

If also a high boiling fraction is isolated in step (c) the separation is preferably performed by means of a atmospheric and vacuum distillation step. In a first distillation at about atmospheric conditions, preferably at a pressure of between 1.2-2 bara, a gas oil product and lower boiling fractions, such as naphtha and kerosine fractions, are separated from the higher boiling fraction of the product of step (b). The higher boiling fraction, of which suitably at least 95 wt% boils above 350 preferably above 370 °C, is subsequently further separated in a vacuum distillation step wherein a vacuum gas oil fraction, the base oil precursor fraction and the higher boiling fraction are obtained. The vacuum distillation is suitably performed at a pressure of between 0.001 and 0.05 bara.

When no higher boiling fraction is isolated in step (c) vacuum distillation step can be omitted. The heavy fraction obtained in the atmospheric distillation step can then be used as base oil precursor fraction.

In step (d) the base oil precursor fraction obtained in step (c) is subjected to a pour point reducing treatment. With a pour point reducing treatment is understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

Preferably step (d) is performed by means of a catalytic dewaxing process. With such a process it has been found that a base oil component having a pour point of below -30 °C and even below -40 °C can be prepared.

The catalytic dewaxing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of

suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

5 The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for  
10 example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a  
15 low acidity refractory oxide binder material, which is essentially free of alumina, is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of  
20 these of which examples are listed above. The most preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is  
25 essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by  
30 contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and  
35 dealuminated Pt/ZSM-23, silica bound and dealuminated

Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-0029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably -10 to below -60 °C.

After performing a catalytic dewaxing step (d) lower boiling compounds formed during catalytic dewaxing are removed, preferably by means of distillation, optionally in combination with an initial flashing step. The remaining fraction can be further separated into one or more base oil products, wherein at least one base oil product is the base oil component having the properties suitable for the automatic transmission fluid of the present invention.

The invention will be illustrated by means of the following non-limiting examples.

#### Example 1

Example 1 illustrates the process to prepare a base oil having a higher cyclo-paraffin content.

A Fischer-Tropsch product was made having boiling curve as in Table 1 by repeating Example VII of WO-A-9934917 using the catalyst as prepared in Example III of the same publication and subsequently removing the C<sub>4</sub> and lower boiling compounds from the

effluent of the synthesis reaction. The feed contained about 60 wt% C<sub>30</sub>+ product. The ratio C<sub>60</sub>+/C<sub>30</sub>+ was about 0.55.

Table 1

Recovered (wt%)	Temperature (°C)
Initial boiling point	82
10	249
30	424
50	553
70	671
90	>750

The Fischer-Tropsch product as thus obtained was continuously fed to a hydrocracking step (step (a)). In the hydrocracking step the Fischer-Tropsch product and a recycle stream consisting of the 370 °C+ fraction of the effluent of step (a) was contacted with a hydrocracking catalyst of Example 1 of EP-A-532118 at a reactor temperature of 330 °C. The Fischer-Tropsch product WHSV was contacted at 0.8 kg/l.h and the recycle stream was contacted at 0.2 kg/l.h at a total pressure of 35 bar and a hydrogen partial pressure of 33 bar. The recycle gas rate was 2000 Nl/kg of total feed. The conversion of compounds boiling above 370 °C in the total feed which were converted to products boiling below 370 °C was 55 wt%. The product of the hydrocracking step was distilled into one or more fuels fractions boiling in the naphtha, kerosene and gas oil range and a bottom product boiling above 370 °C.

The 370 °C+ fraction thus obtained was in turn distilled in a vacuum distillation column, wherein the feed rate to the column was 750 g/h, the pressure at the



top was kept at 0.4 mm Hg (0.5 mbar) and the temperature at the top was kept at 240 °C, which is equal to an atmospheric cut off temperature of 515 °C. The top product had thus a boiling range of between 370 and 515 °C. Further properties were a pour point of +18 °C and a kinematic viscosity at 100 °C of 3.8 cSt. This top product was further used as the base oil precursor fraction in step (c).

In the dewaxing step (c) the base oil precursor fraction was contacted with a dealuminated silica bound ZSM-5 catalyst comprising 0.7% by weight Pt and 30 wt% ZSM-5 as described in Example 9 of WO-A-0029511. The dewaxing conditions were: total pressure 40 bar, a hydrogen partial pressure at the reactor outlet of 36 bar, WHSV = 1 kg/l.h, a temperature of 340 °C and a recycle gas rate of 500 Nl/kg feed.

The dewaxed oil was distilled, wherein a lighter and a heavier fraction was removed to obtain the final base oil having properties as listed in Table 2.

Table 2

Density d20/4	814
Mean boiling point (50 wt% recovered)	430 °C
Kinematic viscosity at 40 °C	18 cSt
Kinematic viscosity at 100 °C	4.0 cSt
Viscosity index	121
Pour point	-50 °C
Noack volatility	11 wt%

Example 4-5

Base oils as prepared from the same feed as in Examples 1 and 2 under varying conditions were prepared. Properties are listed in Table 3. The cyclo-paraffins and normal and iso-paraffins of the base oil of Example 5 (see Table 3) were further analysed. In Figure 1 the content of the components, normal and iso-paraffins, 1-ring cyclo-paraffins, 2-ring cyclo-paraffins, etc. in the saturates phase as a function of their respective carbon numbers are shown of the base oil of Example 5.

Table 3

Base oil type	Example 4	Example 5	Base oil as obtained in Example 2 of EP-A-776959	Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (*)	Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (**)
Viscosity Index	127	121	151	138	132
Pour point (°C)	-48	-54	-19	-21	-39
Kinematic viscosity at 100 °C (cSt)	4.77	4.14	4.80	4.91	4.96
Dynamic viscosity as measured by CCS at -40 °C (cP)	5500	3900	6800	5300	5700
Saturates content (wt%)	99.1	99.9	99.8	99.7	99.6
Total cyclo-paraffin content	13.7	18.5	4.1	6.1	8.2

Table 3 (cont'd)

Base oil type	Exam- ple 4	Exam- ple 5	Base oil as obtained in Example 2 of EP-A- 776959	Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (*)	Base oil as obtained by catalytic dewaxing a Shell MDS Waxy Raffinate over a Pt/synthetic ferrierite catalyst (**)
1-ring cyclo- paraffins (wt%)	11.1	16.8	3.7	4.9	6.4
2-ring cyclo- paraffins	1.4	1.4	0.2	0.5	0.7
3 and higher number rings cyclo-paraffins	1.2	0.3	0.2	0.7	1.1

(\*) Reaction conditions: total pressure 40 bars, WHSV=1 kg/l/h, gas recycle rate = 700 NL/kg feed and temperature of 290 °C.

(\*\*) as in (\*) but at 320 °C dewaxing temperature.

Example 6

A base oil having the properties as in Table 4 and as prepared according to Example 1 using the same Fischer-Tropsch product but at slightly different catalytic dewaxing conditions was formulated with 5 wt% Lubad 924 and 6 wt% of Viscoplex 12-410 to arrive at an Automatic Transmission Fluid (ATF) having the properties as described in Table 5. A minor portion of a second mineral based base oil was added to adjust the base oil kinematic viscosity at 100 °C to 4.03 cSt.

Table 4

Specific Gravity	kg/m <sup>3</sup>	818.5
Flashpoint COC	°C	232
Pour point	°C	- 48
Viscosity at 40 °C	mm <sup>2</sup> /s	20.08
Viscosity at 100 °C	mm <sup>2</sup> /s	4.30
Viscosity Index		122
Brookfield Viscosity		
at - 20 °C	mPa s	550
at - 30 °C	mPa s	1 320
Cyclic-paraffin content	wt%	12.2
Aromatics content	wt%	0.8

Comparative Experiment A

An automatic transmission fluid was formulated using the same additive package as used in Example 4, wherein the base oil component was a blend of 50 wt% Shell XHVI 5.2, 12 wt% MVIN40 (as obtainable from Shell Europe Oil Products) and HVI-50 (as obtainable from Shell Europe Oil Products) balance having a base oil viscosity of 4.03 mm<sup>2</sup>/s at 100 °C. The properties of the resulting formulation are presented in Table 5.

Comparative Experiment B

An automatic transmission fluid was formulated using the same additive package as used in Example 4, wherein the base oil component was a blend of Nexbase 3030 and Nexbase 3043 (as obtainable from Fortum Base Oils, Porvoo, Finland) such that the base had a oil viscosity of 4.03 mm<sup>2</sup>/s at 100 °C. Nexbase is a base oil prepared by a severe hydro-cracking of vacuum gas oil. The properties of the resulting formulation are presented in Table 5.

Comparative Experiment C

An automatic transmission fluid was formulated using the same additive package as used in Example 4, wherein the base oil component was a blend of poly-alpha olefin grade 4 and poly alpha olefin grade 6 (as obtained from Chevron) having a base oil viscosity of 4.03 mm<sup>2</sup>/s at 100 °C. The properties of the resulting formulation are presented in Table 5.

Table 5

Example		6	A	B	C
Base Oil kinematic viscosity at 100 °C	mm <sup>2</sup> /s	4.02	4.03	4.03	4.03
ATF kinematic viscosity at 100 °C	mm <sup>2</sup> /s	6.84	7.2	7.02	6.85
ATF Dynamic viscosity at -40 °C	mPa s	5930	14 000	7860	4800

5       The above table 5 shows that in Example 6 an ATF  
formulation was prepared which had a combination of a low  
kinematic viscosity at 100 °C and a low dynamic viscosity  
at -40 °C comparable to when a poly-alpha olefin base oil  
is used (Comparative experiment C). The advantage of  
using the specific base oil having the high cyclic-  
paraffin content and the other properties as herein  
described over a PAO base oil is the better solvency  
properties of the base oil of Example 6.

10       The results of Example 6 are expected to be even  
better if the base oil would not have been blended with a  
mineral base oil, but instead would have been 100 %  
Fischer-Tropsch derived base oil, such as the base oil as  
prepared in Example 1.

C L A I M S

1. Automatic transmission fluid having a kinematic viscosity at 100 °C of between more than 4 and 10 cSt, a dynamic viscosity at -40 °C of less than 10000 mPas comprising an additive package and a base oil component, wherein the base oil component comprises at least 98 wt% saturates, of which saturates fraction the content of cyclo-paraffins is between 10 and 40 wt% and wherein the pour point of the base oil is less than -25 °C.
2. Fluid according to claim 1, wherein the pour point of the base oil component is below -30 °C.
3. Fluid according to any one of claims 1-2, wherein the VI of the base oil component is between 110 and 150.
4. Fluid according to any one of claims 1-3, wherein the content of cyclic-paraffins is at least 12 wt%.
5. Fluid according to any one of claims 1-4, wherein the base oil component is obtainable from a process comprising the following steps:
  - (a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic Fischer-Tropsch product, which product has a weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product of at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms
  - (b) hydrocracking/hydroisomerising the Fischer-Tropsch product,

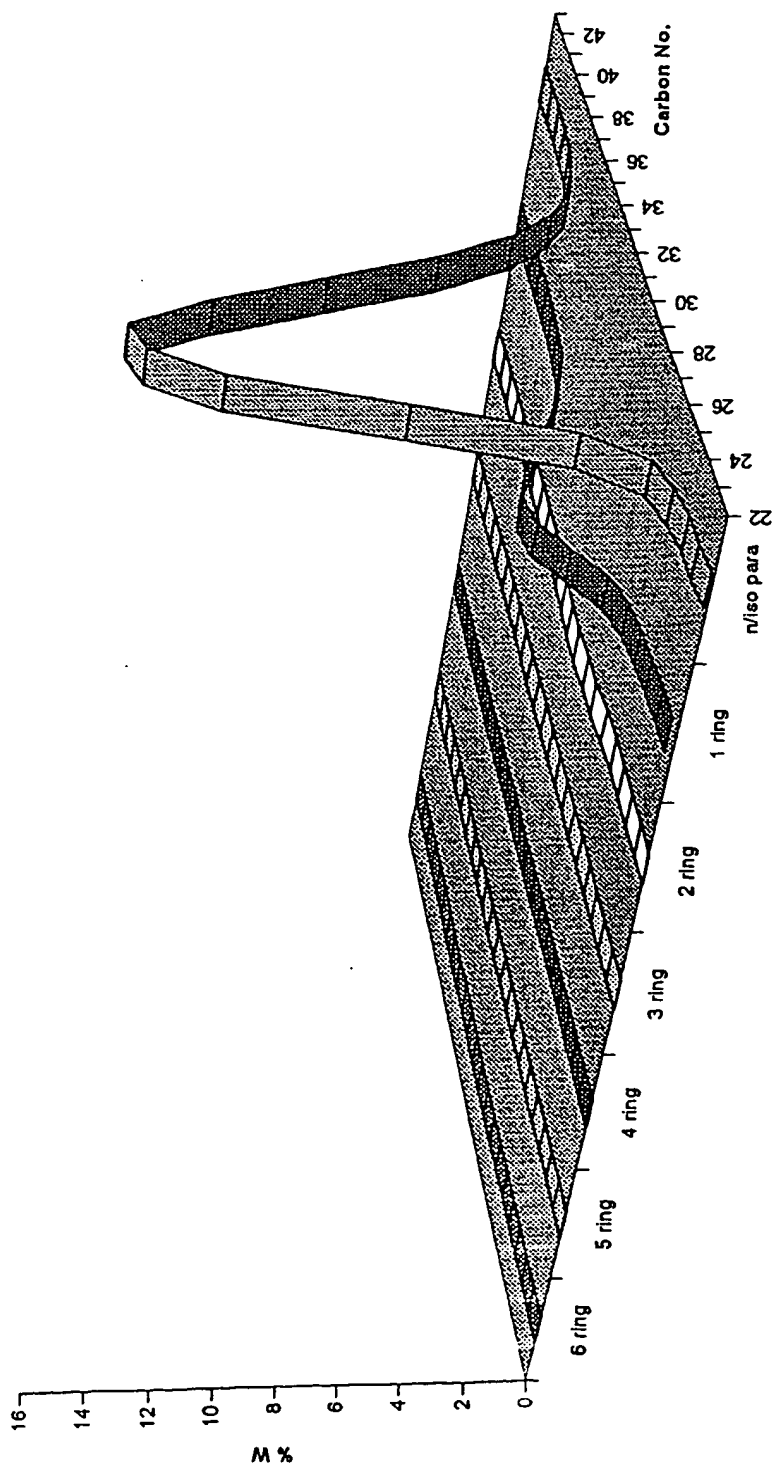


(c) separating the product of step (b) into one or more gas oil fractions, a base oil precursor fraction and a optionally a higher boiling fraction,

5 (d) performing a pour point reducing step to the base oil precursor fraction obtained in step (c), and  
(e) recovering the base oil component from the effluent of step (d).

10 6. Fluid according to claim 5, wherein the Fischer-Tropsch product used in step (b) has at least 50 wt% of compounds having at least 30 carbon atoms and wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is at least 0.4 and wherein the Fischer-Tropsch product comprises a C<sub>20</sub><sup>+</sup>  
15 fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925.

7. Fluid according to claim 6, wherein at least 55 wt% of the compounds have at least 30 carbon atoms.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/02450

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C10M101/02 C10G65/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 059 955 A (CODY IAN A ET AL) 9 May 2000 (2000-05-09) claims 1,2,4 column 4, line 22 - line 27 examples 1,2; tables 1,2	1,3,5
P,A	US 6 255 546 B1 (ALEXANDER ALBERT GORDON) 3 July 2001 (2001-07-03) claims 1,3,6,7	1,2
A	EP 0 994 174 A (CHEVRON USA INC) 19 April 2000 (2000-04-19) claims 1,3,6 table 8	1,2,4
A	WO 00 15736 A (EXXON RESEARCH ENGINEERING CO) 23 March 2000 (2000-03-23) claims 1-15	5
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*G\* document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/02450

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 165 949 A (HABEEB JACOB J ET AL) 26 December 2000 (2000-12-26) claims 1,5,17 -----	5
A	EP 0 776 959 A (SHELL INT RESEARCH) 4 June 1997 (1997-06-04) cited in the application -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/02450

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6059955	A	09-05-2000	AU 742299 B2	20-12-2001
			AU 2765199 A	30-08-1999
			CA 2319531 A1	19-08-1999
			EP 1062305 A1	27-12-2000
			JP 2002503752 T	05-02-2002
			WO 9941332 A1	19-08-1999
US 6255546	B1	03-07-2001	AU 3087201 A	20-08-2001
			WO 0159042 A1	16-08-2001
EP 0994174	A	19-04-2000	US 6110879 A	29-08-2000
			EP 0994174 A1	19-04-2000
WO 0015736	A	23-03-2000	US 6332974 B1	25-12-2001
			AU 5680899 A	03-04-2000
			BR 9913583 A	22-05-2001
			EP 1144551 A2	17-10-2001
			NO 20011245 A	10-05-2001
			WO 0015736 A2	23-03-2000
US 6165949	A	26-12-2000	AU 5690299 A	27-03-2000
			BR 9913410 A	22-05-2001
			EP 1114132 A2	11-07-2001
			NO 20011123 A	02-05-2001
			US 2002086803 A1	04-07-2002
			WO 0014188 A2	16-03-2000
EP 0776959	A	04-06-1997	EP 0776959 A2	04-06-1997
			AU 705415 B2	20-05-1999
			AU 7198896 A	05-06-1997
			CA 2191290 A1	29-05-1997
			CN 1167811 A	17-12-1997
			JP 9221685 A	26-08-1997
			SG 74001 A1	18-07-2000
			TW 416981 B	01-01-2001
			ZA 9609906 A	28-05-1997